

ACTIVITY COEFFICIENTS PREDICTED BY THE LOCAL
COMPOSITION MODEL FOR AQUEOUS SOLUTIONS
USED IN FLUE GAS DESULFURIZATION

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SCOPE

The major objective of this work is to extend the predictability of solution equilibria models for flue gas desulfurization processes by employing an activity coefficient technique which is accurate over a wide concentration range. Current FGD equilibrium models use a Davies technique for activity coefficient prediction. The Davies technique is useful only up to ionic strengths of 1 molal, thus, limiting the application of FGD equilibrium models to low ionic strength. In this work a data base and methods have been developed to use the local composition model (LCM, 1,2) for the prediction of activity coefficients in aqueous FGD solutions. The LCM was used to predict the solubilities in various multicomponent systems for gypsum, calcium sulfite, magnesium sulfite, calcium carbonate, and magnesium carbonate; SO₂ vapor pressure over sulfite/bisulfite solutions; and, CO₂ vapor pressure over carbonate/bicarbonate solutions.

CONCLUSIONS AND SIGNIFICANCE

Accurate prediction of activity coefficients over a 0-6 molal ionic strength range will allow for improvement of available FGD equilibrium models. This will provide accurate equilibrium calculations for low ionic strength lime/limestone processes and higher ionic strength processes as dual alkali or regenerative sodium scrubbing. Additionally, improved accuracy will be available for more complex FGD simulations which use equilibrium models as a means of establishing the inlet scrubber solution composition and to calculate driving forces for rate processes (3).

A data base of necessary binary parameters and equilibrium constants for activity coefficient prediction by the LCM is presented. The LCM has proven to be accurate from 0-6 molal ionic strength for typical FGD aqueous solutions. In general, the LCM is slightly less accurate than the Davies technique from 0-1 molal ionic strength. The advantages of the LCM over the current Davies technique are clearly seen when predicting over the entire concentration range.

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INTRODUCTION

It is often desirable to perform equilibrium calculations in the design or operation of a FGD facility. By using the fundamental principles of conservation of mass and charge, and chemical equilibrium expressions, the concentration of individual species in solution (sometimes called the "species distribution") can be calculated. The available equilibrium models for lime or limestone based FGD are the Bechtel-modified Radian equilibrium program (BMREP, 4) and the species distribution model (SDM, 5). The SDM is the most current equilibrium model and has been improved considerably over earlier models to make it more general in nature. Some simple uses of equilibrium models include predicting the saturation or solubility of gypsum to indicate scaling potential, predicting SO₂ vapor pressure to trouble-shoot problems with SO₂ removal, and predicting dissolved alkalinity or capacity of a solution. However, the BMREP and SDM have limitations which restrict their use to low ionic strength processes.

The practical limit for using the BMREP, SDM, or any equilibrium model for electrolytic solutions normally stems from the lack of correlations for electrolyte thermodynamics (e.g. activity coefficient techniques). The BMREP and SDM currently use the Davies technique for activity coefficient prediction. The Davies technique is a combination of the extended Debye-Huckel equation (6) and the Davies equation (7). The Davies technique (and hence both equilibrium models) is accurate to ionic strengths of 0.2 molal, and may be used for practical calculations up to ionic strengths of 1 molal (8). Ion-pair equilibria are incorporated for species that associate (e.g. 1-2 and 2-2 electrolytes). The activity coefficients (γ_i) are calculated as a simple function of ionic strength (I), and are represented as:

$$\log \gamma_i = A Z_i^2 \left[\frac{-I^{\frac{1}{2}}}{1 + B a_i I^{\frac{1}{2}}} + b_i I \right] \quad 1)$$

where A and B are constants at a given temperature. Depending on the input values of a_i and b_i , Equation 1 can represent either the extended Debye-Huckel or Davies equations, or an extension of the two.

Both the BMREP and SDM approximate activity coefficients of uncharged species (e.g. ion-pairs, molecular species) by the following expression:

$$\log \gamma_i = U_i I \quad 2)$$

where U_i is an empirical constant.

To improve the BMREP and SDM in equilibrium calculations requires an activity coefficient technique which is accurate over a wide concentration range. Rosenblatt (9,10) identified the inherent limitations of the BMREP and SDM, and investigated the use of the modified Pitzer equation as an activity coefficient technique for FGD solutions. The modified Pitzer equation (11-13) was noted as the most elaborate and successful activity coefficient technique in use (14). Rosenblatt concluded that Pitzer's equations offered a promising approach for thermodynamic modeling of FGD chemistry. Currently, Radian is incorporating the Bromley method (15) as a new activity coefficient technique in the SDM (16). Recently, Chen and co-workers (17-19) developed the local composition model (LCM) for activity coefficient prediction. The LCM is a semi-theoretical model with a minimum number of adjustable parameters, and is based on the Non-Random Two Liquid (NRTL) model for nonelectrolytes (20). The LCM does not have the inherent drawbacks of virial-expansion type equations as the modified Pitzer, and proved to be more accurate than the Bromley method. Some advantages of the LCM are that the binary parameters are well defined, have weak temperature dependence, and can be regressed from various thermodynamic data sources. Additionally, the LCM does not require ion-pair equilibria to correct for activity coefficient prediction at higher ionic strengths. Thus, the LCM avoids

defining, and ultimately solving, ion-pair activity coefficients and equilibrium expressions necessary in the Davies technique. Overall, the LCM appears to be the most suitable activity coefficient technique for aqueous solutions used in FGD, hence, a data base and methods to use the LCM were developed.

THE LOCAL COMPOSITION MODEL

The local composition model (LCM) is an excess Gibbs energy model for electrolyte systems from which activity coefficients can be derived. Chen and co-workers (17-19) presented the original LCM activity coefficient equations for binary and multicomponent systems. The LCM equations were subsequently modified and used in the ASPEN process simulator (Aspen Technology, Cambridge, MA) as a means of handling chemical processes with electrolytes. The LCM activity coefficient equations are explicit functions, and require computational methods. Due to length and complexity, only the salient features of the LCM equations will be reviewed in this paper. The "Aspen Plus Electrolyte Manual" (1), and Taylor (21) present the final form of the LCM binary and multicomponent equations.

The approach taken by Chen and co-workers in developing the LCM was to account for the excess Gibbs energy of electrolyte systems as the sum of long-range (ion-ion) interactions, and short-range (ion-ion, ion-molecule, and molecule-molecule) interactions. The extended Debye-Huckel equation proposed by Pitzer (22) was used to account for the long-range interactions, and the local composition concept was used to account for the short-range interactions of all kinds. The excess Gibbs energy expression is therefore the sum of the unsymmetric Pitzer-Debye-Huckel expression and the unsymmetrical local composition expression. The equation has the general form:

$$\frac{g^{ex}}{RT} = \frac{g^{ex,pdh}}{RT} + \frac{g^{ex,lc}}{RT} \quad 3)$$

Similarly, the activity coefficient equations (which can be derived from the excess Gibbs energy expression) have the general form:

$$\ln \gamma_i^* = \ln \gamma_i^{pdh*} + \ln \gamma_i^{lc*} \quad 4)$$

The long-range Pitzer-Debye-Huckel equation calculates activity coefficients as a function of ionic strength, and no adjustable parameters are necessary. The short-range local composition equation calculates activity coefficients by accounting for all short-range interactions, and requires a minimum of adjustable parameters. For binary systems, two adjustable binary parameters are necessary: salt-molecule and molecule-salt. For multicomponent systems three types of adjustable parameters are necessary: salt-molecule, molecule-salt, and salt-salt. Therefore, the regressed parameters of the LCM data base are specifically for the short-range contribution to the activity coefficient equation.

The approach to using the LCM for FGD applications involves some assumptions and simplifications. Since the concentrations of all molecular species in solution are negligible with respect to water, only salt-water and water-salt binary parameters are necessary. All salt-molecule and molecule-salt binary parameters for molecular species other than water are set equal to salt-water and water-salt binary parameters. All molecule-molecule interactions are assumed equivalent to water-water interactions, and are set equal to zero. Additionally, all salt-salt parameters are set to zero. Lastly, the temperature dependence of all binary parameters is neglected.

RESULTS AND DISCUSSIONS

The results of applying the LCM to typical FGD solutions are summarized in tables 1 and 2. Table 1 presents the final regressed LCM binary parameters for typical FGD solutions. The implied formation reactions, and temperature dependent parameters for the equilibrium constants are shown in table 2.

Regression of the necessary LCM binary parameters required various thermodynamic data. The Powell method (23), an unconstrained nonlinear code, was used to minimize a nonlinear function $f(x)=f(x_1, \dots, x_n)$ of n variables. The function $f(x)$ normally represented the standard deviation of the thermodynamic property (e.g. activity coefficients, osmotic coefficients, solubility products, or vapor pressure) being regressed using the LCM for activity coefficient prediction. The n variables represent the final regressed binary parameters. Default values were used for binary parameters representing interactions of species present in low concentration, or when no thermodynamic data were available. Default values were determined by averaging binary parameters regressed by Chen and co-workers (18) for each type of electrolyte (e.g. 1-1, 1-2, 2-1, and 2-2). This approach should yield a minimum error, since the binary parameters are well defined for each type of electrolyte.

The LCM has proven to be useful in predicting data of molal ionic activity coefficients, and vapor pressure depression of various single electrolyte, single solvent systems. The standard deviation of the natural logarithm of the mean activity coefficient was 0.01 for uni-univalent aqueous single electrolytes (17). Similar results were found for uni-bivalent and bi-bivalent electrolyte activity coefficient prediction. Figure 1 compares the LCM with the Davies technique for a sodium sulfate-water system (24). The LCM is accurate over the entire concentration range of 0-6 molal. Two curves are shown for the Davies technique. The upper curve assumes the salt to be totally dissociated, and activity coefficients are calculated directly from Equation 1. The lower curve assumes the ion-pair NaSO_4^- is present, and activity coefficients are calculated from the SDM, which incorporates the additional ion-pair equilibrium. Figure 1 demonstrates the necessity of ion-pair equilibria to insure an accurate activity coefficient prediction in the low concentration range (0-0.2 molal) for salts that associate.

The LCM also predicted activity coefficients of bi-univalent electrolytes (e.g. MgCl_2 and CaCl_2), which exhibit the experimentally observed reversal of slope and dramatic increase in the activity coefficient at higher ionic strengths. For bi-univalent electrolytes, regressing binary parameters over a 0-6 molal range causes some inaccuracy in the low concentration region. However, regressing the LCM binary parameters over a smaller concentration range (0-2.5 molal) improves the LCM accuracy.

The solubility of gypsum in various salt solutions, ranging in ionic strength from 0-6 molal, was predicted accurately by the LCM. Figure 2 compares the LCM and SDM in predicting gypsum solubility with the addition of sodium sulfate at 25, 50, and 75°C (25). A relative saturation of unity would indicate accurate prediction of the experimental data, since the solutions are known to be saturated to gypsum. The LCM predicted the solubility of gypsum in sodium sulfate solutions within 10 percent error in relative saturation at 50 and 70°C, and within 20-30 percent error in relative saturation at 25°C. In magnesium sulfate solutions at 25°C (26), the LCM predicts gypsum relative saturation from 0-6 molal within 30 percent error. The solubility of gypsum in calcium chloride (27) and sodium chloride at 25°C (28) was predicted within 10 percent error in relative saturation from 0-6 molal. In general, the Davies technique, and hence the SDM, gives accurate prediction of gypsum relative saturation only in the low concentration range (0-1 molal). Increasing the ionic strength causes the SDM to yield high relative saturation (as seen in figure 2).

The solubility of magnesium sulfite hexahydrate in water with the addition of magnesium sulfate was accurately predicted by the LCM from 0-6 molal (29). The relative saturation of the magnesium sulfite hexhydrate was predicted within 10 percent error at 40 and 50°C, and within 20 percent error at 60°C.

The LCM accurately predicted the vapor pressure of SO₂ and CO₂ over sulfite/bisulfite and carbonate/bicarbonate solutions, respectively, for salts of sodium, calcium, and magnesium. Figure 3 plots the LCM predictions of SO₂ vapor pressure as a function of the total SO₂ to sodium ratio for a sodium sulfite/bisulfite system at 50°C (30). The LCM was accurate within 20 percent error in SO₂ vapor pressure for the 50°C data, as well as data at 35, 70, and 90°C. The solid line shows the general trend of the LCM predictions. Figure 4 plots the apparent equilibrium constant as a function of ionic strength for a calcium sulfite/bisulfite system at 25, 50, and 60°C (31). The LCM predicts the SO₂ vapor pressure within 6 percent error for this system at all temperatures. Similar results were obtained for a system of magnesium sulfite/bisulfite with the addition of magnesium sulfate at 48.3 and 70.6°C (32). The SO₂ vapor pressure was predicted within 17 percent error for this system. Data for CO₂ vapor pressure analogous to the SO₂ systems discussed are available to a lesser extent. CO₂ vapor pressure over sodium carbonate/bicarbonate solutions (33) from 35-65°C at constant ionic strength (1 molal) were predicted within 10 percent error. CO₂ vapor pressure over calcium (34) and magnesium (35) carbonate/bicarbonate solutions varying in temperature from 25-70°C, and at low ionic strength (< 1.5 molal), were predicted within 5 percent error.

NOTATION

A	Debye-Huckel constant for osmotic coefficient
B	Temperature dependent parameter
I	Ionic strength
R	Gas constant
T	Temperature (°K)
Z	Absolute value of ionic charge
a	Mean distance of closest approach
b	Empirical constant (normally 0.3)
g ^{ex}	Molar excess Gibbs free energy
m	Molality

Greek Letters

γ	Activity coefficient
τ	LCM binary interaction parameter

Subscripts

ca	Salt "ca" of cation c and anion a
m	Molecular species

Superscripts

e	Unsymmetric convention
lc	Short-range local composition contribution
pdh	Long-range Pitzer-Debye-Huckel contribution

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Cation	Anion	$\tau_{ca,m}$	$\tau_{m,ca}$	Data Type	Ref.
H+	SO3-2	-4.667	8.452	D	19
H+	SO4-2	-4.667	8.452	D	19
H+	HSO3-	-4.279	8.489	D	19
H+	CL-	-5.212	10.090	A	24
H+	HCO3-	-4.279	8.489	D	19
H+	CO3-2	-4.667	8.452	D	19
H+	OH-	-4.279	8.489	D	19
H+	HSO4-	-5.448	11.045	V	36
H+	AD-2	-4.667	8.452	D	19
H+	HAD-	-4.279	8.489	D	19
H+	S2O3-2	-4.667	8.452	D	19
H+	S3O6-2	-4.667	8.452	D	19
CA+2	SO3-2	-6.861	11.398	D	19
CA+2	SO4-2	-3.795	7.343	S	25
CA+2	HSO3-	-5.685	11.748	V	31
CA+2	CL-	-4.125	8.319	S	27
CA+2	HCO3-	-6.958	9.467	V	34
CA+2	CO3-2	-6.861	11.398	D	19
CA+2	OH-	-5.799	10.441	D	19
CA+2	HSO4-	-5.799	10.441	D	19
CA+2	AD-2	-6.861	11.398	D	19
CA+2	HAD-	-5.799	10.441	D	19
CA+2	S2O3-2	-4.795	9.542	V	37
CA+2	S3O6-2	-6.861	11.398	D	19
MG+2	SO3-2	-3.857	7.814	S	29
MG+2	SO4-2	-4.205	8.492	S	26
MG+2	HSO3-	-4.137	8.292	V	32
MG+2	CL-	-5.400	11.217	V	37
MG+2	HCO3-	-5.437	10.691	V	38
MG+2	CO3-2	-6.861	11.398	D	19
MG+2	OH-	-5.799	10.441	D	19
MG+2	HSO4-	-5.174	10.044	V	37
MG+2	AD-2	-6.861	11.398	D	19
MG+2	HAD-	-5.799	10.441	D	19
MG+2	S2O3-2	-6.861	11.398	D	19
MG+2	S3O6-2	-6.861	11.398	D	19
NA+	SO3-2	-2.745	5.703	V	30
NA+	SO4-2	-3.830	7.824	A,O,V	36,37,24
NA+	HSO3-	-2.735	7.779	V	30
NA+	CL-	-4.125	6.988	S	28
NA+	HCO3-	-7.196	13.109	V	33
NA+	CO3-2	-4.041	8.077	V	37
NA+	OH-	-4.816	9.644	A,O,V	36,37,24
NA+	HSO4-	-3.987	7.622	V	36,37
NA+	AD-2	-4.667	8.452	D	19
NA+	HAD-	-3.108	5.631	A,O	24
NA+	S2O3-2	-4.218	8.643	A,O,V	36,37,24
NA+	S3O6-2	-4.144	8.214	V	37

Table 1 LCM Data Base: Final Regressed Binary Parameters.
(A-activity coefficient data, D-default parameters,
O-osmotic coefficient data, V-vapor pressure data)

Equilibrium Constant	Implied Formation Reaction	Temperature Dependent Parameters			
		A	B	C	D
Ksp1	CaSO4*2H2O = Ca+2 + SO4-2 + 2H2O	4096.0521	31.3476	0.0	-86.9037
Ksp2	CaSO3* $\frac{1}{2}$ H2O = Ca+2 + SO3-2 + $\frac{1}{2}$ H2O	-4646.4154	31.8594	0.0	100.2073
Ksp3	MgSO3*6H2O = Mg+2 + SO3-2 + 6H2O	8121.4199	54.1774	0.0	-137.5713
Ksp4	MgSO3*3H2O = Mg+2 + SO3-2 + 3H2O	-3181.3288	-16.6579	0.0	55.3001
Ksp5	CaCO3 (calcite) = Ca+2 + CO3-2	13797.9724	108.4748	0.0	-306.2902
Ksp6	MgCO3*3H2O = Mg+2 + CO3-2 + 3H2O	-21134.1076	-143.5699	0.0	431.1240
K1	SO3-2 + SO2(aq) + H2O = 2HSO3-	2280.8682	19.6510	0.0	-60.6891
K2	SO2(aq) + H2O = H+ + HSO3-	276.8176	0.0000	0.006372	0.8521
K3	HSO3- = H+ + SO3-2	-2004.0486	-19.6510	0.006372	61.5412
HSO2	SO2(aq) = SO2(gas)	2422.8421	8.7615	0.0	-29.7136
K4	CO3-2 + CO2(aq) + H2O = 2HCO3-	-147.4864	1.2997	0.0	-6.6947
K5	CO2(aq) + H2O = H+ + HCO3-	5251.5323	36.7816	0.0	-102.2685
K6	HCO3- = H+ + CO3-2	5399.0187	35.4819	0.0	-95.5739
HCO2	CO2(aq) = CO2(gas)	2948.4426	11.4519	0.004540	-41.0371

Table 2 LCM Data Base: Implied Formation Reactions And Temperature Dependent Parameters For Equilibrium Constants. Equation form:

$$-\log K = A/T + B \log T + CT + D$$

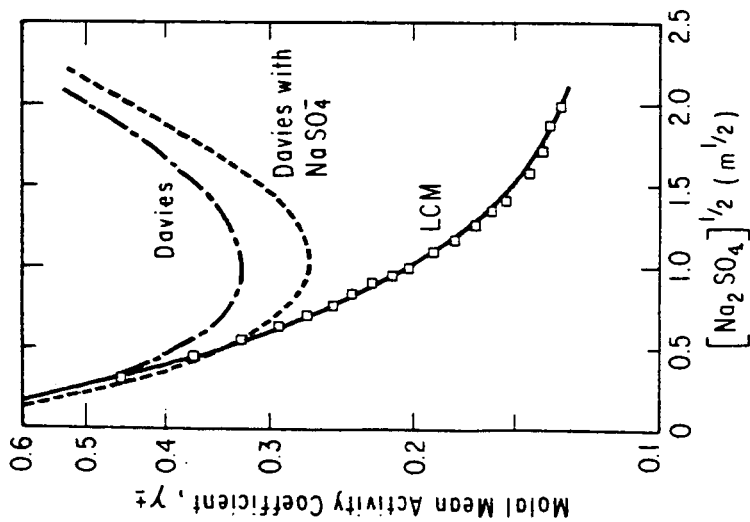


Figure 1 Comparison of SDM Davies Technique and LCM in Predicting Molal Mean Activity Coefficient (1-2 electrolyte) at 25°C. Data from Robinson and Stokes (24).

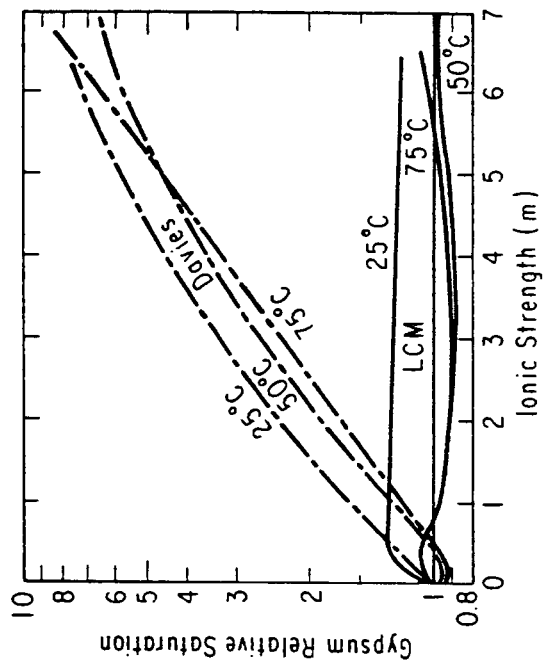


Figure 2 Comparison of SDM Davies Technique and LCM in Predicting Gypsum Relative Saturation with the Addition of Sodium Sulfate. Data from Hill and Wills (25).

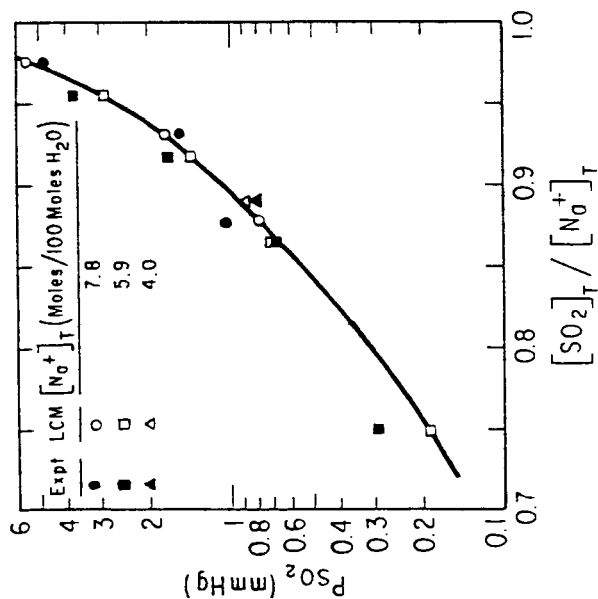


Figure 3 LCM Prediction of SO_2 Vapor Pressure Over Sodium Sulfite/Bisulfite Solutions at $50^\circ C$. Data from Johnstone, et al. (30).

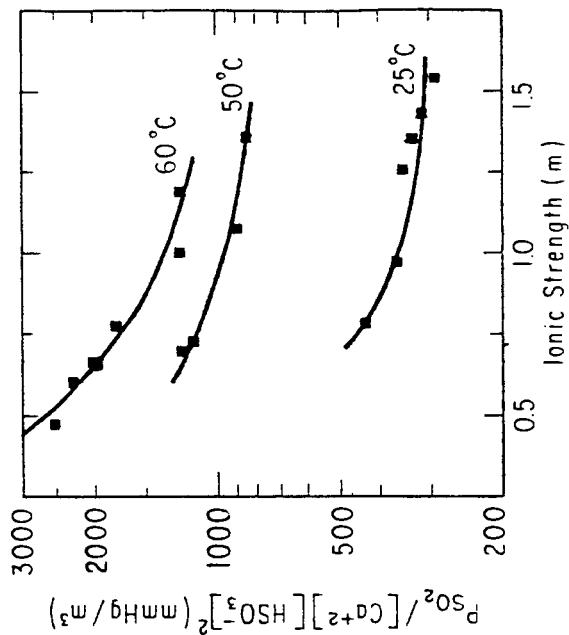


Figure 4 LCM Prediction of Apparent Equilibrium Constant in Calcium Sulfite/Bisulfite Solutions. Data from Kuzminskykh and Babushkina (31).